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METHODS OF REDUCING SKIN IRRITATION ASSOCIATED WITH SHAVING

Background of the Invention

Removal of unwanted body hair has been a regular part of daily grooming for centuries. Shaving is by far the most common method of hair removal for both men and women. It is quick and easy, painless, effective, and inexpensive. The results last only one to three days, however, hence shaving requires a dedicated effort to remain hair-free. Shaving is performed with a razor on wet skin using shaving cream or other lubricants, orienting the razor against the direction of hair growth. For sensitive areas, shaving in the direction of hair growth may reduce cuts. The most common problems associated with shaving are skin irritation, nicks and cuts in the skin, and ingrown hair (*pseudofolliculitis barbae*). Some skin irritation or trauma is unavoidable because some stratum corneum is removed along with the hair and because the skin is degreased and dried by the surfactants used in shaving products.

Control of skin irritation related to shaving is of concern to men and women alike. One of the most effective methods for controlling skin irritation is through the use of an after-shave composition. After-shave compositions are intended to not only to relieve skin irritation but also to provide a cooling and refreshing feeling and impart a mild astringent effect which tightens the skin. They also may act in antimicrobial fashion, reducing the presence of bacteria and thus protecting the skin from infection while it recovers from the mild injury.

Numerous types of after-shave compositions are known. They can take the form of a lotion, gel, quick-breaking foam, or balm and typically contain significant levels of alcohol, which in addition to being antiseptic provides a cooling and astringent effect and enhances the drying rate of the composition when applied to skin. The presence of alcohol also serves to prevent contamination of the

composition by microorganisms, both during manufacture and storage and after the composition's container is opened and put into use.

Prior art compositions have sought to eliminate the stinging associated with the use of volatile alcohols by reducing the amount of alcohol 5 present, which also reduces or eliminates the beneficial effects of alcohol. Conversely, anhydrous compositions which combine 20% to 50% alcohol with 40% to 70% low viscosity silicone fluids are claimed to have less stinging and burning although at significantly higher cost than alcohol/water compositions.

Known methods of reducing irritation and improving skin condition 10 include incorporation of active therapeutic ingredients into after-shave compositions. Such active ingredients include aloe vera, aluminum chlorhydrate, chamomile combined with niacinamide, non-steroidal anti-inflammatory agents, and panthenol. The use of hydrolyzed soy protein in combination with cocamidopropyl dimethylamine propionate is also known.

15 Other methods of reducing skin irritation associated with shaving are sought.

Summary of the Invention

This invention provides methods of reducing skin irritation 20 associated with shaving (i.e., before, during, and/or after shaving) facial hair or nonfacial hair. The methods include applying to skin various formulations, which typically are preservative-free, have good application aesthetics, provide immediate cooling and skin tightening, evaporate quickly, have a pleasant fragrance, and leave the skin looking and feeling smooth and soft after both single and multiple 25 applications. Additionally, preferred formulations maintain or improve the skin condition after multiple applications and no slimy or abnormal feeling is noticed during post application washing.

In one method of reducing skin irritation associated with shaving, the method includes applying to skin a composition that includes:

30 a) a lower alcohol and water in a weight ratio of about 20:80 to 100:0, and
b) about 0.5% to about 8% by weight of a thickener system, based on the total weight of the composition, wherein the thickener system comprises

at least about 0.05% by weight of at least one emulsifier, based on the total weight of the composition, wherein the emulsifier comprises:

- (i) at least one hydrophobic group selected from the group consisting of:
 - A. an alkyl group of at least 16 carbon atoms;
 - B. an alkenyl group of at least 16 carbon atoms; and
 - C. an aralkyl or an aralkenyl group of at least 20 carbon atoms; and
- (ii) at least one hydrophilic group selected from the group consisting of:
 - A. an ethylene oxide- and/or propylene oxide-containing group bonded to the hydrophobic group through an ether or ester bond and optionally terminated with a (C1-C36)alkyl ester, (C2-C36)alkenyl ester, or (C6-C36)alkaryl ester;
 - B. an alcohol group;
 - C. a polyhydric alcohol group;
 - D. an ester or ether group of a polyhydric alcohol or polyalkoxylated derivative thereof having 2-150 moles of alkylene oxide per mole of hydrophobic group;
 - E. an ester or ether group of sorbitan or polyalkoxylated derivative thereof; and
 - F. combinations of these groups;

wherein the composition has a viscosity of at least about 4,000 centipoise at 23°C

when in the absence of an auxiliary thickener, as measured using a very low shear viscometer and T spindles with a heliopath adapter.

In one method of reducing skin irritation associated with shaving, the method includes applying to skin a composition that includes:

- a) a lower alcohol and water in a weight ratio of about 20:80 to 100:0, and
- b) about 0.5% to about 8% by weight of a thickener system, based on the total weight of the composition, wherein the thickener system comprises

at least about 0.05% by weight of at least one emulsifier, based on the total weight of the composition, wherein the emulsifier comprises:

- (i) at least one hydrophobic group selected from the group consisting of:
 - 5 A. an alkyl group of at least 24 carbon atoms;
 - B. an alkenyl group of at least 24 carbon atoms; and
 - C. an aralkyl or an aralkenyl group of at least 24 carbon atoms; and
- (ii) at least one hydrophilic group selected from the group consisting of:
 - 10 A. an ethylene oxide- and/or propylene oxide-containing group bonded to the hydrophobic group through an ether or ester bond and optionally terminated with a (C1-C36)alkyl ester, (C2-C36)alkenyl ester, or (C6-C36)alkaryl ester;
 - B. an alcohol group;
 - C. a polyhydric alcohol group;
 - D. an ester or ether group of a polyhydric alcohol or polyalkoxylated derivative thereof having 2-150 moles of alkylene oxide per mole of hydrophobic group;
 - E. an ester or ether group of sorbitan or polyalkoxylated derivative thereof; and
 - 15 F. combinations of these groups;

wherein the composition has a melt temperature of greater than about 25°C and a viscosity of at least about 4,000 centipoise at 23°C when in the absence of an auxiliary thickener, as measured using a very low shear viscometer and T spindles with a heliopath adapter.

In one method of reducing skin irritation associated with shaving, the method includes applying to skin a composition that includes:

- 30 a) a major amount of a solvent comprising a lower alcohol and water in a weight ratio of about 60:40 to 95:5, and

5 b) about 0.5% to about 8% by weight of a thickener system, based on the total weight of the composition, wherein the thickener system comprises at least about 0.05% by weight of one or more emulsifiers, based on the total weight of the composition, wherein at least one of the emulsifiers is solid at room temperature;

wherein the composition has a melt temperature of greater than about 25°C and a viscosity of at least about 45,000 centipoise after 19 days at 23°C when in the absence of an auxiliary thickener, as measured using a very low shear viscometer and T spindles with a heliopath adapter.

10 In one method of reducing skin irritation associated with shaving, the method includes applying to skin a composition that includes:

- a) a lower alcohol and water in a weight ratio of about 20:80 to 100:0, and
- b) about 0.5% to about 8% by weight of a thickener system, based on the total weight of the composition, wherein the thickener system comprises at least about 0.05% by weight of at least two emulsifiers, based on the total weight of the composition, wherein at least one emulsifier comprises:
 - (i) at least one hydrophobic group selected from the group consisting of:
 - A. an alkyl group of at least 16 carbon atoms;
 - B. an alkenyl group of at least 16 carbon atoms; and
 - C. an aralkyl or an aralkenyl group of at least 20 carbon atoms; and
 - (ii) at least one hydrophilic group selected from the group consisting of:
 - A. an ethylene oxide- and/or propylene oxide-containing group bonded to the hydrophobic group through an ether or ester bond and optionally terminated with a (C1-C36)alkyl ester, (C2-C36)alkenyl ester, or (C6-C36)alkaryl ester;
 - B. an alcohol group;

In one method of reducing skin irritation associated with shaving, the method includes applying to skin a composition that includes:

30 a) a lower alcohol and water in a weight ratio of about 20:80 to 95:5; and
b) about 0.5% to about 8% by weight of a thickener system, based on the total weight of the composition, wherein the thickener system comprises at

least about 0.05% by weight of at least one emulsifier, based on the total weight of the composition, wherein the emulsifier comprises:

(i) at least one hydrophobic group selected from the group consisting of:

- A. an alkyl group of at least 16 carbon atoms;
- B. an alkenyl group of at least 16 carbon atoms; and
- C. an aralkyl or an aralkenyl group of at least 20 carbon atoms; and

(ii) at least one hydrophilic group selected from the group consisting of:

- A. an amide group;
- B. a short chain ester of a long chain alcohol or acid;
- C. a polyglucoside group having 1-10 glucose units;
- D. a polyglycerol ester group having 1-15 glycerol units;
- E. a secondary amine group;
- F. a tertiary amine group;
- G. a anionic group;
- H. a zwitterionic group; and
- I. combinations of these groups;

20 wherein the composition has a viscosity of at least about 4,000 centipoise at 23°C when in the absence of an auxiliary thickener, as measured using a very low shear viscometer and T spindles with a heliopath adapter.

Definitions

25 "After-shave" as used herein refers to a lotion, gel, cream, foam, stick, balm, or mousse that is applied to skin. The term is also understood to include compositions applied prior to, during, or after shaving which may facilitate the shaving process by improving the shave, reducing irritation, adding lubricity, disinfecting, reducing discomfort of any kind, and any combination thereof.

30 "Ambient temperature" as used herein refers to the temperature range between about 21°C and 25°C (i.e., of about 21°C to about 25°C).

"Auxiliary thickeners" as used herein refers to additives (other than the emulsifiers which comprise the thickener system described below), which increase the viscosity of the solvent phase even in the absence of the thickener system. Certain auxiliary thickeners may act synergistically with the thickener system to increase the viscosity of the resultant formula. Auxiliary thickeners include but are not limited to soluble and swellable polymers (e.g. polyacrylic acid polymers such as CARBOPOL, BF Goodrich, Cleveland, OH) and associative colloidal thickeners such as silica, magnesium aluminum silicate, and the like.

"Emollient" as used herein refers broadly to materials which are capable of maintaining or improving the moisture level, compliance, or appearance of the skin when used repeatedly.

"Emulsifier" as used herein is synonymous with "surfactant" and refers to molecules comprising hydrophilic (polar) and hydrophobic (non-polar) regions on the same molecule.

15 "Emulsion" as used herein refers to a stable dispersion of one liquid
in a second immiscible liquid.

"Lotion" means liquid or cream, free of any propellant.

"Melt temperature" (Tm) as used herein refers to the temperature at which compositions or emulsions of the present invention dramatically lose viscosity.

"Polymer" as used herein refers to a natural or synthetic molecule having repetitive units and a number average molecular weight of at least 20,000.

"Solvent," "solvent system" or "hydroalcoholic solvent" as used herein refer to the alcohol and water combination in the present invention.

25 "Stable" as used herein refers to a composition that displays less than
or equal to 10% by volume separation after centrifuging at 2275 x g for 30 minutes
at ambient temperature.

"Surfactant" as used herein is synonymous with "emulsifier," the definition of which is given above.

30 "Thickener system" as used herein refers to a combination of at least one emulsifier, and preferably at least two emulsifiers, each present in a concentration of at least 0.05% by weight capable of providing a viscosity of at least

4,000 centipoise at 23°C to the compositions used in the methods of the present invention without auxiliary thickeners.

Detailed Description of Preferred Embodiments

5 The invention provides methods of reducing skin irritation associated with shaving using a composition that includes a lower chain alcohol, water, and thickening system. Alcohols used in these compositions are first discussed followed by a discussion of thickening systems. Ingredients that are optionally added to the composition, such as emollients, are then discussed, followed by a discussion of
10 how to prepare compositions used in the methods of the present invention.

Alcohol

15 The alcohol used in the compositions is a lower hydrocarbon chain alcohol such as a C1-C4 alcohol. In preferred embodiments the alcohol is chosen from ethanol, 2-propanol, or n-propanol, and most preferably ethanol. Ethanol is a preferred alcohol for certain embodiments since it has an odor acceptable to consumers. The invention anticipates that a single alcohol may be used or that a blend of two or more alcohols may form the alcohol content of the composition.

20 The alcohol to water ratio in the compositions used in the methods of the present invention is between about 20:80 and 100:0 by weight (i.e., within a range of about 20:80 to about 100:0). Compositions having alcohol to water ratios below about 20:80 fail to provide much benefit in terms of rapid evaporation or cooling. Preferred compositions have alcohol to water ratios within the range of about 35:65 (and more preferably 40:60) to about 95:5 by weight range. In an even
25 more preferred embodiment the alcohol:water ratio is between about 50:50 and 85:15, more preferably between about 60:40 and about 75:25, and most preferably the alcohol:water ratio is between about 64:36 and 72:28 by weight. Higher alcohol to water ratios are used in a preferred embodiment for optimum antimicrobial activity and to ensure the composition is fast drying.

Thickener System

The thickener system useful in the compositions used in the methods of the invention affects the cosmetic attributes of the final composition. Preferably, compositions of the invention should maintain an acceptable viscosity at 25°C and 5 preferably up to 35°C. Also, the most preferred formulations are stable to heat and cool cycles (heating up to 50°C or higher and cooling to ambient temperature) as well as freeze/thaw cycles (cooling to -30°C and warming to ambient temperature). These attributes are affected by the types and amounts of emulsifiers chosen which form the thickener system of the present invention and are discussed below.

10 The thickener system is compatible with the hydroalcoholic solvent system described above in order to provide acceptable cosmetic properties and appropriate viscosity. Compositions of this invention have a viscosity of at least about 4,000 Centipoise (cps) at 23°C, preferably at least about 10,000 cps, more preferably at least about 20,000, even more preferably at least about 50,000 cps, 15 even more preferably at least about 90,000 cps, and most preferably at least about 100,000 cps, and preferably up to about 500,000 cps, measured using a very low shear viscometer such as Brookfield LVDV-I⁺ viscometer and T spindles with a heliopath adapter. Since the emollient system and other optional ingredients may affect the viscosity (either positively or negatively), the measured viscosity is that of 20 the final composition without any added auxiliary thickeners.

The viscosity of the compositions used in the methods of the present invention is imparted by a thickener system that includes at least one emulsifier, preferably at least two emulsifiers, and more preferably at least two emulsifiers from different classes. In a preferred embodiment at least one of the emulsifiers is a solid 25 at room temperature. Such emulsifier preferably includes at least one long chain hydrocarbon of at least 16 carbon atoms, preferably at least 18 carbon atoms, and more preferably at least 22 carbon atoms. At lower alcohol:water ratios of greater than about 60:40, the long chain hydrocarbon preferably has greater than 22 carbon atoms. The thickener system can be described in terms of the number average chain 30 length, and preferably has a hydrophobe number average chain length of greater than about 22 carbon atoms.

Emulsifiers used in the compositions of this invention are comprised of molecules having hydrophilic (polar) and hydrophobic (non-polar) regions on the same molecule and conform to the general structure:

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$(R)_a(L)_b$

wherein "R" represents a hydrophobic group, "L" represents a hydrophilic group, and "a" and "b" are independently 1 to 4.

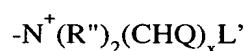
In this invention "R" comprises an alkyl group of at least about 16 carbon atoms, preferably at least about 18 carbon atoms, more preferably at least about 20 carbon atoms, and most preferably at least about 22 carbon atoms; alkenyl group of at least about 16 carbon atoms, preferably at least about 18 carbon atoms, and most preferably at least about 20 carbon atoms; or aralkyl or aralkenyl group of at least about 20 carbon atoms, preferably at least about 24 carbon atoms, and most preferably at least about 26 carbon atoms. In a preferred embodiment the alkyl or alkenyl portion of "R" is unbranched.

In the above formula, "L" represents a hydrophilic group. For example, "L" can include an amide group having the structure $-NHC(O)R'$ or $-C(O)NHR'$ where R' is hydrogen or an alkyl group of 1-10 carbon atoms optionally substituted in available positions by N, O, and S atoms; an ester group of short chain alcohols or acids (e.g., $L = -C(O)OR'$ or $-OC(O)R'$ where R' is C1-C4 branched or straight chain alkyl optionally substituted in available positions by hydroxyl groups); a polyglucoside group having 1-10 glucose units and more preferably 1-3 glucose units; a polyglycerol ester group having 1-15 glycerol units, preferably 2-12 glycerol units, and more preferably 3-10 glycerol units; a secondary amine group; a tertiary amine group; and a quaternary amine group.

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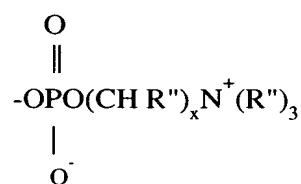
"L" can also include an anionic group such as a sulfate, sulfonate, phosphate, phosphonate, or carboxylate group, or a zwitterionic group having the formula:

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or

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15 wherein each R'' is independently hydrogen or an alkyl group (having 1-5 carbon atoms) or alkenyl group (having 2-4 carbon atoms), which alkyl or alkenyl groups are optionally substituted with nitrogen, oxygen, or sulfur atoms, including alkyl or alkenyl carboxyl groups; Q is hydrogen or hydroxyl; x is 1 to 4; and L' is
-CO₂⁻, -OP(O)(O⁻)(O⁻M⁺), -(O)P(OR'')(O)(O⁻) (where R'' is hydrogen or an alkyl
20 group of 1-10 carbon atoms optionally substituted in available positions by N, O, or S atoms), -SO₂O⁻, or -OSO₂O⁻, where M⁺ is a positively charged counterion present in a molar ratio necessary to achieve a net neutral charge on the emulsifier and is selected from the group of hydrogen, sodium, potassium, lithium, ammonium, calcium, magnesium, or N⁺R''₄.

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"L" can also include an alcohol group; a polyhydric alcohol group such as, but not limited to, ethylene glycol, butylenes glycol, pentaerythrytol, glycerol, and sorbitol; an ethylene oxide and/or propylene oxide group, preferably having 2-150 moles of ethylene oxide plus propylene oxide per mole of hydrophobe ("R"), which is bonded to the hydrophobe through an ether or ester linkage, and
30 optionally terminated by C1-C36 alkyl, C2-C36 alkenyl ester, or C6-C36 alkaryl ester (i.e., aralkyl ester); an ester or ether group of a polyhydric alcohol and their polyalkoxylated derivatives; an ester or ether of sorbitan or polyalkoxylated (i.e., polyalkyleneoxide) sorbitan group, preferably having 2-150 moles of alkylene oxide units per mole of hydrophobe; as well as combinations of these groups, e.g., a

polyethoxylated polyglucoside group. Thus, it will be understood by one of skill in the art that the emulsifiers can include combinations of all "L" hydrophilic groups described herein (e.g., ester groups and amide groups in one molecule).

5 The hydrophobic and hydrophilic groups on non-ionic emulsifiers are generally selected to have a hydrophile/lipophile balance (HLB) of 2 to 20 and more preferably 4 to 16. Furthermore, the weight average HLB of the thickener system is preferably 4 to 16 and more preferably 8 to 12. For example, a thickener system comprised of 40% by weight of an emulsifier with an HLB of 10 and 60% by weight of an emulsifier with an HLB of 15 has a weight average HLB of 13.

10 The emulsifiers of the thickener systems may be chosen from a single class of surfactants (e.g., a mixture of chain length alkyl polyglucosides) but is preferably a mixture of emulsifier classes. Many commercially available emulsifiers are actually comprised of a mixture of chain lengths. For example, some behenyl alcohol as commercially supplied is actually a mixture of alcohols

15 consisting of primarily C22 and C20 fractions but contain detectable levels of C24, C18 and C16 fractions. For this reason, the chain lengths specified herein refer to the number average chain length. Furthermore, in multiple emulsifier thickener systems, each emulsifier must be present in a concentration of at least about 0.05% and more preferably at least about 0.1% by weight to be considered a component of

20 a thickener system. Thickener systems of the present invention are capable of achieving high viscosities at relatively low total emulsifier concentrations. The total concentration of emulsifiers present as a thickener system for creams and lotions is generally less than about 8% by weight, preferably less than about 5% by weight, more preferably less than about 4% by weight, and most preferably less than about

25 3% by weight of the total composition. Typically, the thickener system is present in the composition in an amount of at least about 0.5 % by weight, based on the total weight of the composition. In the most preferred lotion compositions of this invention, the thickener system comprises between about 0.75% by weight to about 5% by weight, more preferably between about 1.0% by weight to about 3.5% by

30 weight and most preferably between about 1.5% by weight to about 3% by weight of the composition. As used herein an emulsifier is considered part of the thickener system if its presence in the formula results in an increase in the viscosity of the

composition. If a certain emulsifier does not result in increasing the viscosity of the composition, it is considered an emollient or stabilizer as defined below.

Preferred methods of the present invention include compositions that are substantially free of polymeric thickening agents and have a "melt temperature" (T_m). If compositions are heated above this melt temperature, they dramatically lose viscosity. The compositions preferably have melt temperatures greater than 25°C in order to maintain a high viscosity at room temperature. More preferably the melt temperature is greater than 35°C in order to maintain viscosity once applied to the skin. The most preferred formulations have a melt temperature greater than 10 40°C in order to allow shipping and handling without refrigeration. Thickener systems affect the melt temperature of a given composition. In order to obtain a preferred melt temperature a preferred thickener system includes at least one emulsifier, which is solid at ambient temperature. Preferably, all emulsifiers of a thickener system are solid at ambient temperature to increase the melt temperature 15 of the resultant composition.

The structure of emulsifiers in a thickener system affects the melt temperature of the resultant composition. In a preferred embodiment at least one emulsifier in a thickener system is capable of promoting a crystalline structure. Crystallinity is promoted by long straight chain alkyl groups, therefore, at least one 20 emulsifier preferably comprises a saturated straight chain hydrocarbon of at least 16, preferably at least 18 and most preferably at least 20 carbon atoms. Certain hydrophilic head groups have been found to particularly promote association and crystallization. Suitable crystalline emulsifiers include alkyl alcohols, alkyl polyglucosides, polyglycerol alkyl esters, C1-C4 esters of alkyl alcohols, C1-C4 25 esters of alkyl carboxylates, optionally substituted alkyl amides, alkyl betaines and alkyl phosphates or phospholipids, alkyl quaternary amines, alkyl amine oxides polyethoxylated alkyl alcohols and alkyl esters of polyethylene glycol.

In addition to affecting the melt temperature of a composition, the emulsifier chain length also helps to determine the maximum level of ethanol which 30 can be used in the composition and the concentration of emulsifiers required in the thickener system. At higher levels of alcohol, longer chain emulsifiers are required to produce viscous stable emulsions. It is believed that higher levels of alcohol tend

to swell or solubilize the emulsifiers to a greater degree than lower levels of alcohol. Therefore, as the concentration of ethanol increases the chain length of the hydrocarbon chains in a thickening system must also increase in order to maintain a melt temperature over 35°C. That is, the amount of lower alcohol in the

5 hydroalcoholic system can affect the choice of surfactant (i.e., emulsifier), and vice versa. For example, if the composition includes a lower alcohol to water ratio in excess of about 50:50, the thickener system should include at least one surfactant having a number average chain length of at least 16 carbon atoms. If the composition includes an alcohol to water ratio in excess of about 60:40, the

10 thickener system should include at least one surfactant having a number average chain length of at least 18 carbon atoms. If the composition includes a lower alcohol to water ratio in excess of about 64:36, the thickener system should include at least one surfactant having a number average chain length of at least 20 carbon atoms.

15 For example, systems based on a C16/C18 alkyl polyglucoside (MONTANOV 68 available from Seppic, Inc. of Fairfield, NJ) in combination with a C18 polyethoxylate (BRIJ 76 available from ICI of Wilmington, Delaware) in 68:32 ethanol:water have a melt temperature of approximately 35°C. Similar systems having C22 hydrocarbon chains have melt temperatures of 45°C or higher.

20 In addition, as the chain length of the hydrophobic component in the thickener system increases, the amount of emulsifier required to achieve a certain viscosity decreases. For example, the MONTANOV 68 (C16/C18 alkyl polyglucoside)/BRIJ 76 (polyethoxylated C18 alcohol) thickener system requires approximately 5% total emulsifier to achieve a suitable viscosity. A similar system based on C22

25 hydrophobes achieves a suitable viscosity at only 2% total emulsifier.

The nature and size of hydrophilic head groups of emulsifiers are important and help to determine which thickening systems produce viscous stable systems. Certain combinations of emulsifiers will produce viscous stable emulsions. Without being bound by theory, it is believed that the size, charge, and

30 degree of hydrogen bonding are important parameters to determine how emulsifiers interact.

Many preferred thickener systems are capable of producing viscoelastic compositions, which are very stable. By varying the ratio of emulsifiers, the degree of elasticity can be adjusted from almost a purely viscous composition to a highly elastic and even stringy composition. If emollients are 5 added, increasing the elasticity of the system imparts added stability to prevent separation of immiscible emollients. Excessive elasticity, however, is not preferred since an elastic composition usually does not provide a cosmetically appealing product. Addition of certain emulsifiers with at least two hydrophobic components has been shown to limit the viscoelasticity while ensuring viscous stable 10 compositions. A favored class of multiple hydrophobic component emulsifiers are quaternary ammonium salts conforming substantially to the following structure:



where: R' and R'' are long chain alkyl or alkenyl hydrocarbon chains of at least 16 20 carbon atoms;

R''' is a short chain alkyl group of 1 to 4 carbon atoms, preferably methyl or ethyl;

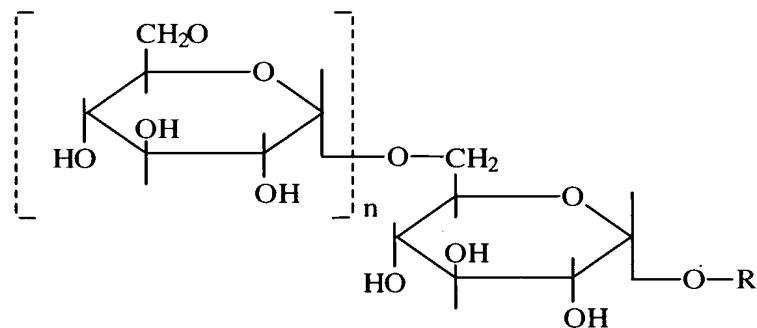
R'''' is equivalent to either R' or R'' and is preferably equivalent to R'''; and

25 X is a halogen, R'''SO₃⁻, R'''SO₄⁻, or R'''CO₂⁻

Some preferred structures include distearyldimethylammonium chloride, dibehenyldimethylammonium chloride, and dibehenyldimethylammonium methosulfate, while dibehenyldimethylammonium methosulfate is a more preferred structure. Other suitable multiple hydrophobic emulsifiers include dialkylglycerol 30 esters, trialkylglycerol esters, polyglycerol alkyl esters, ethylene glycol dialkylesters, polyethylene glycol dialkylesters, dialkylamides of diamines such as ethylene diamine, polyalkylesters of pentaerythritol and dialkyl (optionally ethoxylated) phosphates, and alkyl esters of polyethoxylated alkyl alcohols.

The following emulsifier classes are offered as nonlimiting examples of suitable emulsifiers for use in the present invention. Examples of some preferred emulsifiers are provided for each emulsifier class.

5 *Class 1. Alkyl or Alkenyl Polyglucosides:*



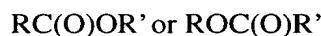
where R is a straight chain alkyl or alkenyl group of at least 16 carbon atoms, preferably at least 18 carbon atoms, and most preferably at least 20 carbon atoms; or an aralkyl or aralkenyl group of at least 22 carbon atoms, preferably at least 24

10 carbon atoms and most preferably at least 26 carbon atoms; and n = 0-10 (when n = 0, the valence of the oxygen atom is completed by H), preferably 1-5 and more preferably 1-3.

Nonlimiting examples of preferred alkyl or alkenyl polyglucoside emulsifiers include cetearyl glucoside sold as MONTANOV 68 by Seppic, Inc. of 15 Fairfield, New Jersey; behenyl glucoside, produced experimentally as ESSAI 624 MP, an alkyl polyglucoside prepared with 92% C-22 alcohol and corn-derived glucoside by Seppic, Inc.; and oleyl glucoside.

Class 2. Short Chain Esters of long chain Alcohols or Acids:

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where R is as defined immediately above for Emulsifier Class 1; and

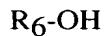
R' is C1-C4 branched or straight chain alkyl group, optionally substituted in available positions by hydroxyl groups.

Some preferred short chain esters of long chain alcohols or acids include but are not limited to methyl behenate sold as KEMESTER 9022 by

5 Crompton Corp., Greenwich, CT; methyl stearate sold as KEMESTER 4516 by Crompton Corp.; methyl oleate sold as KEMESTER 205 by Crompton Corp.; arachidyl propionate available as WAXENOL 801 from Alzo of Sayreville, NJ; behenyl lactate, stearyl acetate; and glycerol monoerucate available from Croda, Inc. of Parsippany, NJ.

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Class 3. Alkyl and Alkenyl Alcohols:



where R_6 is a straight or branched chain alkyl or alkenyl hydrocarbon chain of at

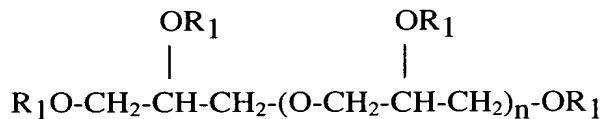
15 least 16 carbon atoms, preferably at least 18, more preferably at least 20 carbon atoms, and most preferably at least 22 carbon atoms, optionally substituted in available positions by N, O, or S atoms; or an aralkyl or aralkenyl group of at least 16 carbon atoms, preferably at least 22 carbon atoms, more preferably at least 24 carbon atoms, and most preferably at least 26 carbon atoms, optionally substituted

20 in available positions by N, O, and S atoms.

Nonlimiting examples of preferred alkyl and alkenyl alcohol emulsifiers useful in a thickener system of the invention include stearyl alcohol available as LANETTE 18 from Henkel's Emery Division of Cincinnati, Ohio; behenyl alcohol available as LANETTE 22 from Henkel; oleyl alcohol available as

25 NOVOL from Croda; C-24 alcohol available as UNILIN 350 from Petrolite of Tulsa, Oklahoma; C31 alcohol available as UNILIN 425 from Petrolite; and arachidyl alcohol available as AR-20 from M. Michel and Co. of New York, NY.

Class 4. *Polyglycerol Ester*

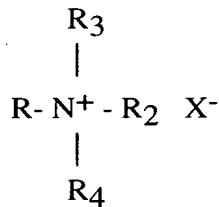


5

where each R_1 is independently hydrogen or a straight chain alkyl group of at least 16 carbon atoms, preferably at least 18 and more preferably at least 20 carbon atoms; or an aralkyl or aralkenyl group of at least 22 carbon atoms, preferably at least 24 carbon atoms, and most preferably at least 26 carbon atoms; and $n = 0$ to 10, preferably 1 to 12, and most preferably 2 to 10.

Some examples of preferred polyglycerol ester emulsifiers useful in a thickener system of the present invention include but are not limited to decaglycerol monostearate available as POLYALDO 10-1-S from Lonza Inc. of Fairlawn, NJ; tetraglycerol monostearate available as TETRAGLYN 1-S from Barnet Products Corporation of Englewood Cliffs, NJ; and decaglyceroltetrabehenate.

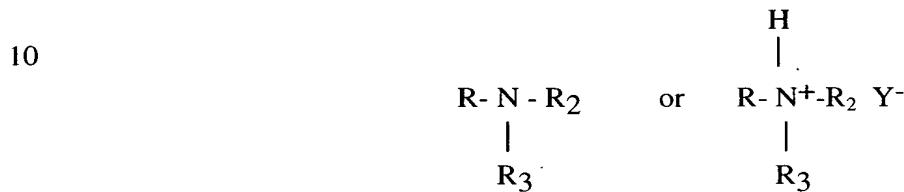
Class 5. *Quaternary Amine*



20 where R is as defined above in Emulsifier Class 1; R_2 is the same as R_3 or a long chain alkyl or alkenyl hydrocarbon chain of at least 16 carbon atoms, preferably at least 18 and more preferably at least 20 carbon atoms optionally substituted in available positions by N, O, and S; or an aralkyl or aralkenyl group of at least 22 carbon atoms, preferably at least 24 carbon atoms, and most preferably at least 26 carbon atoms; R_3 is a short chain alkyl group of 1 to 4 carbon atoms, preferably methyl or ethyl; R_4 is equivalent to either R_2 or R_3 and is preferably equivalent to R_3 ; and X is a halogen, R_5SO_3^- , R_5SO_4^- , R_5CO_2^- , $(\text{R}_5)_2\text{PO}_4^-$, or $(\text{R}_5)\text{PO}_4^{=}$; where R_5 is defined in Class 6 below.

Nonlimiting examples of quaternary amine emulsifiers include dibehenyldimethylammonium methosulfate available as INCORQUAT DBM-90 from Croda; behenyltrimethylammonium chloride available as NIKKOL CA-2580 from Barnet; and tallowtrimethylammonium chloride available as ARQUAD T-5 27W from Akzo Chemicals, Inc. of Chicago, IL.

Class 6. Tertiary Amine and its Protonated salts



15 where R, R₂, and R₃ are as defined above in Class 5 and R₂ and R₃ may also be selected from polyethoxylated or polypropoxylated alkyl or alkenyl alcohol chains having 1-50 moles of ethylene oxide or propylene oxide groups per mole of emulsifier and Y is a halogen, R₅SO₃⁻, R₅SO₄⁻, R₅CO₂⁻, (R₅)PO₄⁻, or (R₅)PO₄⁼, where R₅ is an alkyl or alkenyl group of 1-22 carbon atoms optionally substituted in 20 available positions by N, O, and S.

Some examples of emulsifiers from the class of tertiary amines and their protonated salts useful in a thickener system of the invention include but are not limited to behenamidopropyldimethylamine available as INCROMINE BB from Croda; behenamidopropyldimethylamine gluconate; tallowdimethylamine hydrochloride; dihydrogenated tallow methyl amine; stearyl diethanolamine hydrochloride; polyethoxylated stearyl diethanolamine hydrochloride.

Class 7. Amine Oxides

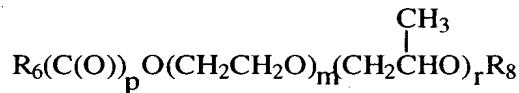


where R_2 and R_3 are as defined above for Class 5 and R_6 is as defined above for Class 3.

Nonlimiting examples of emulsifiers from the class of amine oxides 5 suitable in a thickener system of the invention include behenamine oxide (behenyldimethylamine oxide) available as INCROMINE B-30P from Croda; stearamine oxide available as INCROMINE Oxide S from Croda; behenamidopropyldimethyl amine oxide; and bis(2-hydroxyethyl)tallow amine oxide available as AROMOX T/12 from Akzo.

10

Class 8. Polyethoxylated and/or Polypropoxylated Alcohols and Esters and Derivatives thereof



where R_6 is as defined above for Emulsifier Class 3; $m = 0-200$, preferably 2-50,

15 most preferably 4-20;

$p = 0$ or 1;

$R_8 = H$ or $-C(O)-R_{12}$,

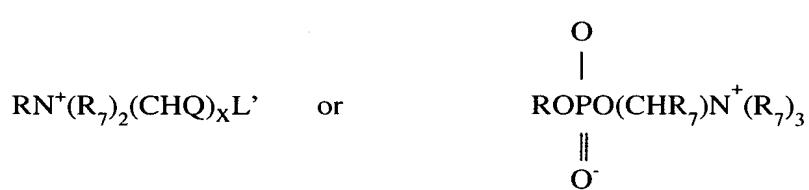
where R_{12} is an alkyl or alkenyl group of 1-36 carbon atoms optionally substituted by N, O or S, or an aralkyl group of 6 to 36 carbon atoms; and

20 $r = 0-50$.

Some examples of preferred emulsifiers from the class of polyethoxylated alcohols and esters include but are not limited to steareth-2 available as BRIJ 72 from ICI Americas Inc. of Wilmington, DE; steareth-10 available as BRIJ 76 from ICI; beheneth-5 available as NIKKOL BB-5 from Barnet Products Inc.; beheneth-10 25 available as NIKKOL BB-10 from Barnet; C31 alkyl-10EO available as UNITHOX 450 from Petrolite Corp. of Tulsa, OK; C31 alkyl-40 EO available as UNITHOX 480 from Petrolite, and the lauric ester of UNITHOX 480 available from Petrolite as X-5171.

Class 9. Zwitterionics

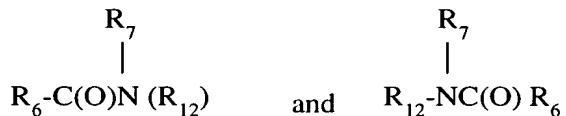
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wherein R is as defined above for Emulsifier Class 1; each R₇ is independently hydrogen or an alkyl group (having 1-5 carbon atoms) or alkenyl group (having 2-4 carbon atoms), which alkyl or alkenyl groups are optionally substituted with nitrogen, oxygen, or sulfur atoms, including alkyl or alkenyl carboxyl groups; Q is hydrogen or hydroxyl; x is 1 to 4; and L' is -CO₂⁻, -OP(O)(O⁻)(OM⁺), -(O)P(OR'')(O)(O⁻) (where R'' is hydrogen or an alkyl group of 1-10 carbon atoms optionally substituted in available positions by N, O, or S atoms) -SO₂O⁻, or -OSO₂O⁻, where M⁺ is a positively charged counterion present in a molar ratio necessary to achieve a net neutral charge on the emulsifier and is selected from the group of hydrogen, sodium, potassium, lithium, ammonium, calcium, magnesium, or N⁺R'₄, where each R' is independently an alkyl group of 1 to 4 carbon atoms optionally substituted with N, O, or S atoms.

20 Nonlimiting examples of emulsifiers from the class of zwitterions useful in the emulsifier system of the invention include stearamidopropylPG-dimmonium chloride phosphate available as PHOSPHOLIPID SV from Uniqema of Paterson, NJ; and behenyl betaine available as INCRONAM B-40 from Croda.

25 *Class 10. Alkyl and Alkenyl Amides*



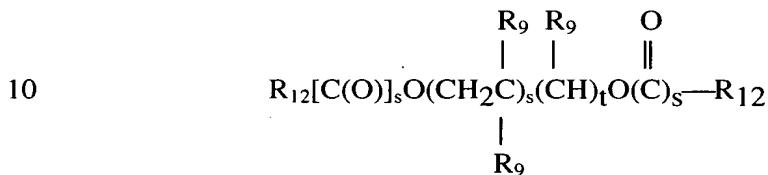
30 where R₆, R₇, and R₁₂ are as defined above in Classes 3, 9, and 8 respectively.

Examples of some preferred emulsifiers from the class of alkyl and alkenyl amides useful in a thickener system of the invention include but are not limited to behenamide available as KEMAMIDE B from Crompton Corp.;

stearamide available as UNIWAX 1750 from Petrolite; Behenamidopropyldimethyl amine available as INCROMINE BB from Croda; stearyl diethanolamide available as LIPAMIDE S from Lipo Chemicals Inc. of Paterson, NJ; and Erucamide available as ARMID E from Akzo.

5

Class 11. Esters and Ethers of Polyhydric Alcohols

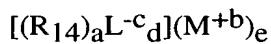


wherein $t = 0-4$; each R_9 is independently chosen from H , $-\text{CH}_2\text{OR}_{10}$, $-\text{OH}$, or a hydrocarbon chain of 1 to 4 carbon atoms, preferably containing 1 carbon atom; $s = 15$ 0 or 1; wherein $\text{R}_{10} = \text{H}$, R_8 , or R_{12} wherein R_8 and R_{12} are defined above for Emulsifier Class 8.

Examples of esters and ethers include glycerol monobehenate, pentaerythritol distearate and glycerol tribehenate.

20 Esters and ethers of polyethoxylated polyhydric alcohols are also useful. For example, these include but are not limited to polyethoxylated glycerol monostearate, polyethoxylated penta erythritol behenate, polyethoxylated propylene glycol monostearate.

25 *Class 12. Anionics*



where R_{14} is an alkyl, alkenyl, or aralkyl group of at least 16 carbon atoms, 30 preferably at least 18 carbon atoms and most preferably at least 20 carbon atoms optionally comprising oxygen, nitrogen, or sulfur atoms within or substituted upon the alkyl or alkenyl chain; or a polyethoxylated and/or polypropoxylated alkyl, alkenyl or aralkyl group, which alkyl, alkenyl, or

aralkyl group comprises at least 16 carbon atoms, preferably at least 18 carbon atoms and most preferably at least 20 carbon atoms optionally comprising oxygen, nitrogen, or sulfur atoms within or substituted upon the alkyl, alkenyl, or aralkyl chain. When R₁₄ comprises a polyethoxylated or

5 polypropoxylated substituent or a copolymeric substituent of ethylene oxide and propylene oxide, these subunits are present in amounts of 1 to 100 moles, preferably 1 to 20 moles per mole of hydrophobe; L is sulfate (—OSO₂O[—]), sulfonate (—SO₂O[—]), phosphate ((—O)₂P(O)O[—] or

—OP(O)(O[—])₂), or carboxylate (—CO₂[—]); M is hydrogen (H⁺), sodium

10 (Na⁺), potassium (K⁺), lithium (Li⁺), ammonium (NH₄⁺), calcium (Ca⁺²), magnesium (Mg⁺²), or R" A⁺, wherein R" is hydrogen or an alkyl or cycloalkyl group of about 1 to 10 carbon atoms, and A⁺ is selected from the group consisting of N^{+(R)3} (e.g., R" A⁺ can be N^{+(CH₃R)4},

HN^{+(CH₂CH₂OH)₃, H₂N(CH₂CH₂OH)₂) or a heterocyclic -N⁺B wherein}

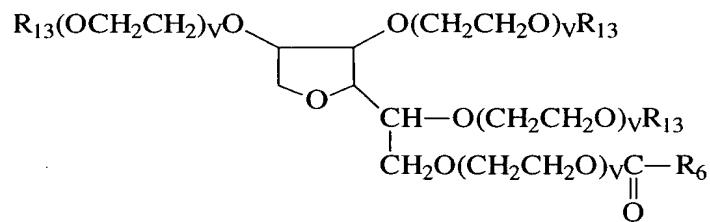
15 B comprises 3 to 7 atoms selected from the group consisting of carbon, nitrogen, sulfur and oxygen atoms which complete the nitrogen-containing heterocyclic ring and satisfy the valence on the nitrogen atom; and wherein R is the same as R" and may also be substituted in available positions with oxygen, nitrogen or sulfur atoms; a and c are independently 1 or 2;

20 b and d are independently 1, 2 or 3; and e is equal to (c times d)/b.

Nonlimiting examples of preferred emulsifiers from the anionic class of emulsifiers suitable for use in a thickener system of the invention include behenic acid available as Croacid B from Croda, Inc.; stearyl phosphate available as Sippostat 0018 from Specialty Industrial Products, Inc. of Spartanburg, SC; and

25 sodium stearate available from Crompton Corp..

Class 13. Sorbitan Fatty Acid Esters



5 where R_6 is as defined above in Emulsifier Class 3, R_{13} is H or $-\text{C}(\text{O})\text{R}_6$ and each
v is independently 0-30.

10 Fatty acid esters of sorbitan and its polyethoxylated derivatives,
polyoxyethylene derivatives of mono and poly-fatty esters are also examples of
additional emulsifiers useful in the present invention.

Certain combinations of the above-listed emulsifiers are useful in
some preferred embodiments to form viscous stable thickener systems of the present
invention. These preferred systems are listed below.

Nonlimiting Examples of Suitable Thickener Systems:

<u>System #</u>	<u>Emulsifier 1 /Class)*</u>	<u>Emulsifier 2 /Class)*</u>	<u>Emulsifier 3 /Class)*</u>	<u>Emulsifier 4 /Class)*</u>
1	Alkyl polyglucoside (1)	polyethoxylated alkyl alcohol (8)	quaternary amine (5)	
2	alkyl polyglucoside (1)	polyethoxylated alkyl alcohol (8)	amine Oxide (7)	
3	alkyl polyglucoside (1)	tertiary amine (6)		
4	alkyl polyglucoside (1)	quaternary amine (5)		
5	polyglycerol ester (4)	polyethoxylated alkyl alcohol (8)	alkyl alcohol (3)	
6	polyglycerol ester (4)	polyethoxylated alkyl alcohol (8)	alkyl alcohol (3)	alkyl ester (2)
7	polyglycerol ester (4)	polyethoxylated alkyl alcohol (8)	quaternary amine (5)	
8	polyglycerol ester (4)	alkyl ester (2)	quaternary amine (5)	
9	polyglycerol ester (4)	amine oxide (7)	quaternary amine (5)	
10	alkyl/alkenyl alcohol (3)	alkyl ester (2)	quaternary amine (5)	
11	alkyl/alkenyl alcohol (3)	alkyl ester (2)	amine oxide (7)	
12	alkyl ester (2)	polyethoxylated alkyl alcohol (8)	quaternary amine (5)	
13	alkyl betaine (7)	polyethoxylated alkyl alcohol (8)		
14	alkyl phospholipid (9)	polyethoxylated alkyl alcohol (8)		
15	alkyl ester (2)	alkyl alcohol (3)		dialkoxydimethicone
16	hydroxyfunctional ester (2)	polyethoxylated alcohol (8)		
17	hydroxyfunctional ester (2)	alkyl alcohol (3)	quaternary amine (5)	
18	hydroxyfunctional ester (2)	quaternary amine (5)		
19	polyglycerol ester (4)	polyethoxylated alkyl alcohol (8)		
20	alkyl carboxylate (12)	polyethoxylated alkyl alcohol (8)		

*Refers to Emulsifier Classes identified above.

It is a simple matter to test certain combinations of emulsifiers to determine if they provide a suitable thickener system. Screening methodology is set forth in the Examples. The examples illustrate the importance of the head group size 5 with respect to the ratio of the mixed emulsifiers required to produce a stable emulsion. For example, systems based on a C16/C18 alkyl polyglucoside combined with C18 polyethoxylates of varying level of ethoxylation (BRIJ) produce stable emulsions at widely varying ratios.

Without intending to be bound by theory, the physical structure of the 10 compositions used in the methods of the present invention is believed to be that of an emulsion. A classic definition of an emulsion is a stable dispersion of one liquid in a second immiscible liquid. However, as stated earlier, the present composition is preferably formed using at least one emulsifier that is a solid wax at room temperature. The compositions described herein are believed to be a viscous stable 15 mixture of a solid, semisolid, or liquid phase in a second liquid phase. It is believed that if certain hydrophobic emollients are added to the compositions, hydrophobic emulsifiers and immiscible emollients form an "oil" or hydrophobic phase which is dispersed in the hydroalcoholic liquid phase to form an "oil" in "water" emulsion. The hydroalcoholic phase is referred to herein as the "water" phase. Since many 20 preferred emulsions are somewhat viscoelastic, these emulsions are believed to be liquid crystalline emulsions that have been cooled below the crystallization temperatures of the chosen emulsifiers to form a semi-crystalline gel-like network. Certain formulations may be simply swollen crystalline precipitates forming a 25 strongly interacting network in the hydroalcoholic phase (so called coagel phase). The compositions described herein may also exist as combinations of these structures. Liquid crystalline and coagel phases in aqueous systems are described in "Application of Emulsion Stability Theories to Mobile and Semisolid O/W Emulsions," *Cosmetics and Toiletries*, Vol. 101, pp 73-92 (1986), and "Influence of Long Chain Alcohols (or Acids) and Surfactants on the Stability and Consistencies 30 of Cosmetic Lotions and Creams," *Cosmetics and Toiletries*, Vol. 92, pp. 21-28 (1977) both of which are hereby incorporated by reference. The exact type of

molecular association that occurs depends on many factors including the nature, size, and physical and chemical states of the polar and hydrocarbon portions of the emulsifiers that form the thickener system at a specified temperature.

Certain of these liquid crystalline or coag gel phases interact with

- 5 light in such a way as to provide a pearlescent or opalescent appearance. The resulting rainbow effect aesthetically enhances the appearance of the formulation without added dyes or pigments.

Emulsifiers other than those required in the composition to provide a thickener system may also be added as emollients or stabilizers. These emulsifiers

- 10 are referred to herein as auxiliary emulsifiers. For example, certain emollients are also comprised of hydrophobic and hydrophilic regions and are useful in the present invention since they are believed to become incorporated into the liquid crystalline network. These emollients tend to enhance the stability of the composition as is discussed more fully below. Furthermore, certain dimethicone copolyol surfactants
- 15 can actually improve the stability of formulations incorporating emollients. This is also discussed in more detail below.

Optional Ingredients

In addition to alcohol, water and thickener system, the compositions

- 20 of the present invention may optionally include ingredients such as salts, emollients, stabilizers, antimicrobials, fragrances, therapeutic agents, propellants and additional emulsifiers. Each of these optional ingredients along with the effect each has upon the properties of the final composition is discussed below.

25 *Salts*

The melt temperature of the compositions used in the methods of the present invention may be increased by adding salts. As the concentration of salt is increased, the ratio of emulsifiers will often need to change in order to maintain a stable composition. It is important to choose salts that do not create an unstable

- 30 system.

Stabilizers

A stable composition is one that does not separate more than 10% by volume after centrifuging at 2275 x g for 20 minutes as measured at the longitudinal midpoint of the sample tube. It is also recognized that stability may be time dependent due to crystallization of emulsifiers and/or emollients present in the system, coalescence of emollients, emulsifiers and the like and, therefore, preferred compositions do not exhibit separation of more than 10% after standing for 6 months at ambient conditions. Two types of stabilizers are useful in the present invention. These include (1) those stabilizers that complex with emulsifier hydrophilic head groups, and (2) those that associate with the emulsifier hydrophobic tails. Certain stabilizers may perform both functions. For example, emulsifiers comprising 1,2 diol-containing head groups such as alkylpolyglucosides, monoalkylglycerides, and polyglycerol alkyl esters, may be "stabilized" by adding borate ion. Without intending to be bound by theory, it is believed that borate ions complex with adjacent head groups which may increase the association of hydrophobic tails by holding them in close proximity. Natural or synthetic polymers comprised of pendent long chain alkyl groups (greater than 12 and preferably greater than 16 carbon atoms) such as stearyl modified cellulose derivatives, stearyl modified proteins such as wheat protein, stearyl modified collagen and the like are capable of stabilizing compositions of the present invention. Such added components may also increase the melt temperature of compositions of the present invention. It is believed that the pendent alkyl groups in these polymers associate by Van der Waals interactions with the hydrophobes of a thickening system, thereby enhancing the stability of the crystalline structure. Polymeric thickeners that do not have associative pendent alkyl chains may also increase the melt temperature presumably by increasing the viscosity of the continuous phase. A nonlimiting example of such thickeners are quaternary celluloses such as CELQUAT 230M as available from National Starch of Bridgewater, New Jersey. In a preferred embodiment stearidimonium hydroxypropyl cellulose commercially available as CRODACEL QS from Croda Inc., Parsippany, NJ is added as a stabilizer.

Emollients

Emollients are typically added to hand and body lotions because they act to increase the moisture content of the stratum corneum. Emollients are generally separated into two broad classes based on their function. The first class of 5 emollients function by forming an occlusive barrier to prevent water evaporation from the stratum corneum. The second class of emollients penetrate into the stratum corneum and physically bind water to prevent evaporation. The first class of emollients is subdivided into compounds that are waxes at room temperature and compounds that are liquid oils. The second class of emollients includes those that are 10 water soluble and are often referred to as humectants.

For the purposes of this invention the thickener system is considered separate and distinct from any emollients which may be added even though it is recognized that the emulsifiers may function as occlusive emollients and aid in maintaining or improving the skin condition. Emollients are included in a preferred 15 embodiment of the invention and preferably comprise between about 3 and 30%, more preferably between about 4 and 20% and most preferably between about 5 and 12% by weight of the formulation.

The ratio of wax to liquid emollients (oils and humectants) in a preferred embodiment of the invention is between about 5:1 to 1:5 and preferably 20 between about 1:3 to 3:1. Also, the ratio of wax emollients and wax emulsifiers to liquid emollients and liquid emulsifiers in a preferred embodiment of this invention is from about 1:5 to about 5:1, and more preferably, from about 1:3 to about 3:1. Emollients may be selected from any of the classes known in the art. A general list of useful emollients appears in U.S. Pat. No. 4,478,853 and EPO patent application 0 25 522 624 A1 and in the *CTFA Cosmetic Ingredient Handbook* published by The Cosmetic, Toiletry, and Fragrance Association, Wash. D.C. (1992) under the listings "Skin Conditioning Agents," "Emollients," "Humectants," "Miscellaneous" and "Occlusive."

In preferred embodiments, emollients are chosen from the following 30 nonlimiting list of general emollients, occlusive emollients and humectants.

Examples of general emollients include short chain alkyl or aryl esters (C1-C6) of

long chain straight or branched chain alkyl or alkenyl alcohols or acids (C8-C36) and their polyethoxylated derivatives; short chain alkyl or aryl esters (C1-C6) of C4-C12 diacids or diols optionally substituted in available positions by -OH; alkyl or aryl C1-C9 esters of glycerol, pentaerythritol, ethylene glycol, propylene glycol, as well

5 as polyethoxylated derivatives of these and polyethylene glycol; C12-C22 alkyl esters or ethers of polypropylene glycol; C12-C22 alkyl esters or ethers of polypropylene glycol/polyethylene glycol copolymer; and polyether polysiloxane copolymers. In addition to many of the emulsifiers of preferred thickener systems, additional examples of occlusive emollients include cyclic dimethicones,

10 polydialkylsiloxanes, polyaryl/alkylsiloxanes, long chain (C8-C36) alkyl and alkenyl esters of long straight or branched chain alkyl or alkenyl alcohols or acids; long chain (C8-C36) alkyl and alkenyl amides of long straight or branched chain (C8-C36) alkyl or alkenyl amines or acids; hydrocarbons including straight and branched chain alkanes and alkenes such as squalene, squalane, and mineral oil; polysiloxane

15 polyalkylene copolymers, dialkoxy dimethyl polysiloxanes, short chain alkyl or aryl esters (C1-C6) of C12-C22 diacids or diols optionally substituted in available positions by OH; and C12-C22 alkyl and alkenyl alcohols. Nonlimiting examples of preferred humectant type emollients include glycerol, propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, pantothenol, gluconic acid salts and the like.

20

Although a thickener system is responsible for the stability and overall consistency of compositions of the present invention, emollients may also affect the viscosity, stability, and melt temperature of a composition. It is anticipated that a single emollient may be added to the present invention or two or more

25 emollients may be added to the composition. A wide range of emollients may be added to the formulations of the present invention. Preferably wax and oil type emollients along with water soluble emollients are used. In a preferred embodiment, emollient systems are comprised of humectants in addition to occlusive wax and oil emollients in concentrations which achieve a moisturizing but not greasy

30 composition which maintains and improves the condition of the skin upon repeated

use. Preferably, emollients are non-comedogenic, non-acnegenic, and are chosen to ensure no skin irritation or sensitization reaction occurs.

Without being bound or limited by theory, it is believed that if emollients are added to the present compositions, they may be present in four distinct regions. The emollients could occur (1) as a soluble species in the solvent phase, (2) dispersed as emulsified droplets within the mixed emulsifier micelle or crystalline gel network, (3) incorporated into the mixed emulsifier micelle or crystalline gel network, or (4) as a separate and distinct emulsion. As earlier stated, emollients can affect the melt temperature of a composition. Those emollients that are soluble or dispersible in the solvent phase tend to have little or no affect on the melt temperature and are therefore preferred. These emollients include the humectant and general emollients. The most preferred general emollients are those which are essentially insoluble in water but soluble in the hydroalcoholic solvent. These emollients are also preferred since they remain soluble and uniformly dispersed even above the melt temperature so that upon cooling to room temperature a uniform composition results. Such general emollients typically do not have alkyl or alkenyl chains greater than about 14, preferably not greater than 12 and most preferably not greater than about 9 carbon atoms.

Those emollients which are insoluble in the hydroalcoholic solvent may associate with the emulsifiers of the thickener system and/or become incorporated into the micelle or crystalline gel network. Preferred emollients within this class are those emollients that are very hydrophobic since they tend to maintain a high melt temperature. For example, hexadecane was found to increase the viscoelasticity of certain thickener systems. Those emollients which are capable of associating with and disrupting the emulsifiers of the thickener system tend to decrease the melt temperature and may influence the stability of the composition. Certain branch alkyl esters of greater than about 12 carbon atoms per hydrophobe have been found to be particularly effective at decreasing the melt temperature. For example, trioctyldodecyl citrate has been found to significantly decrease the melt temperature of some systems.

Emollients which become incorporated into the thickener system tend to decrease the melt temperature. For example, laureth-4 (BRIJ 30) appears to incorporate into the thickener system since it does not phase out when heated above the melt temperature at concentrations below about 1% by weight. Laureth-4 also 5 tends to decrease the melt temperature of the composition.

Certain emollients which are insoluble in the hydroalcoholic solvent can be emulsified in what is believed to be a separate and distinct emulsion. These emollients have little affect on the melt temperature of a composition. For example, certain cyclic silicones, polysiloxanes, and dialkoxypolysiloxanes can be emulsified 10 in hydroalcoholic solvents using polyether/polysiloxane copolymers surfactants. Cyclic silicones such as DC344 (available from Dow Corning of Midland, Michigan) in the presence of certain polyether/polysiloxane copolymers such as ABIL B88183 available from Goldschmidt Chemical Corp. of Hopewell, VA., can form a thermally stable emulsion such that the compositions remain uniform both above and below 15 the melt temperature. In fact, the combination of a long chain dialkoxypolysiloxane and polyether/polysiloxane copolymer has been found to actually promote the stability of certain thickener systems. The dialkoxypolysiloxane is believed to interact with the thickener system as well as the polyether/polysiloxane copolymer. These compounds have the following structures:

20

Dialkoxo dimethicones



25 where R is a straight chain alkyl group of 14-50, preferably 16-24 carbon atoms, and
 $z = 5-300$

Polyether/polysiloxane Copolymers (Dimethicone Copolyols)

30 $(CH_3)_3-Si-O-[Si(CH_3)R_{11}-O]_x[Si(CH_3)R_8-O]_y-Si(CH_3)_3$

where $x + y = 5-400$, preferably 15-200, and
R₈ is a polyether substituted alkyl group with the structure:
-R₉-O(C₂H₄O)_p(C₃H₆O)_qR₁₀;
where R₉ is an alkyl group of 1 to 6 carbon atoms;
5 R₁₀ is hydrogen or an alky group of 1-22 carbon atoms;
R₁₁ is an alkyl group of 1 to 22 carbon atoms or phenyl;
p = 2-300, preferably 8-100; and
q = 0-100.

10 Note that branched chain polysiloxanes modified as shown in the two structures above are also possible.

The following are nonlimiting examples of emulsifier/emollient components which improve thickening/stability of compositions of the present invention.

15 a. Certain wax emulsifiers/emollients have been found to be particularly useful and include solid waxy esters such as: Myristyl Myristate, Cetyl Palmitate, Myristyl Stearate, Stearyl Behenate, Behenyl Isostearate, Isostearyl Behenate, Behenyl Behenate, Lauryl Behenate, Behenyl Erucate. These have the following formula:

20 R₁-CO₂-R₂ where: R₁ is at least 14 carbon atoms; and
R₂ is an alkyl or alkenyl of at least 4 carbon atoms.

25 b. Long chain hydrocarbon di-esters, tri-esters, of polyhydric alcohols with melting point greater than 23°C include solid esters such as glycerol tribehenate and sorbitan tristearate.

- c. Pure lanolins and lanolin derivatives (e.g. hydrogenated lanolin) provide excellent emolliency and can also improve the stability of the emulsion when used in combination with oil emollients.
- 5 d. Petrolatums provide excellent emolliency and can also improve the stability of the emulsion when used in combination with oil emollients. Petrolatums are mixtures of oily and waxy long chain hydrocarbons.
- 10 e. Microcrystalline waxes and branched hydrocarbon waxes with a melting point greater than 50°C and a molecular weight greater than 400. An example of this includes but is not limited to VYBAR 103 which is a branched hydrocarbon with a number average molecular weight of 2800 and is available from Petrolite Corp. of Tulsa, OK and ULTRAFLEX which is a microcrystalline wax also available from Petrolite Corp.
- 15 f. Oxidized waxes and modified hydrocarbon waxes may find application in the present invention. These are prepared from waxes modified by oxidation, salts of oxidized waxes, maleic anhydride adducts of polyolefins and urethane derivatives of oxidized synthetic or petroleum waxes. Applicable waxes could include Petrolite's Cardis or Petronauba microcrystalline and polyethylene-based oxidized products, Polymekon (salts) and Ceramer (anhydride adducts).
- 20 g. Fully saturated homopolymers of polyethylene or copolymers of various alkene monomers may be used to form polymers with a molecular weight at or below 3,000 with a melting point below 130°C and low melt viscosities. Applicable waxes could include POLYWAX available from Petrolite Corp.

Fragrances

The formulations may also include a fragrance. If fragrances are included the fragrances must be chosen carefully since some fragrances are known to cause skin irritation and/or sensitization reactions.

One or more fragrances can be used in compositions of this invention in amounts ranging from about 0.5 to about 8%, preferably from about 1 to about 4% by weight. A fragrance formulation may include such components as C10-C30 terpenes, C5-C50 aldehydes, C5-C50 ketones, C5-C50 esters and combinations thereof. Preferred fragrances are liquids at room temperature and are relatively volatile having a closed cup flashpoint of less than 120C and preferably less than 95C when tested according to ASTM D-56 "Standard Method for Flashpoint by Tag Closed Tester." The following is a list of illustrative specific fragrance components: iso-amyl salicylate, carvacrol, clove leaf oil, ethyl salicylate, iso-eugenol, hexyl 5 salicylate, thyme oil red, geraniol, limonene, 6-acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene, p-t-amyl cyclohexanone, 2-n-heptylcyclo-pentanone, a-iso-methyl ionone, beta-methyl naphthyl ketone, iso-butyl quinoline, methyl anthranilate, o-t-butylcyclohexyl acetate, p-t-butylcyclohexyl acetate, diethyl phthalate, nonanediol-1,3-diacetate, nonanolide-1,4, i-nonyl acetate, i-nonyl formate, 10 phenylethyl phenyl acetate, cinnamic alcohol, dimyrcetol, hydroxymethyl isopropyl cyclopentane, tetrahydromuguol, cedar wood oil, geranyl phenylacetate, guaiacwood oil, linalyl benzoate, phenyl ethyl alcohol, dihydromyrcenol, linalool, isolongifolanone, hexyl cinnamic aidehyde, linalyl acetate, citronellyl acetate, phenyl ethyl acetate, acetyl tributyl citrate, benzyl salicylate, isobutyl cinnamate, linalyl 15 cinnamate, coumarin, acetyl cedrene, allyl amyl glycolate, vanillin, patchouli oil, bergamot oil, citronellol, and combinations thereof. The nomenclature adopted for the components listed above, so far as possible, is that employed by Steffan Arctander in "Perfume and Flavor Chemicals (Aroma Chemicals)" Volume I and II (1969) and the "Perfume & Flavor Materials of Natural Origin" (1960) by the same 20 author.

Foams

The compositions used in the methods of the present invention may also be formulated into an aerosol foam or mousse by addition of an appropriate 30 propellant. The propellant must be chosen to ensure proper delivery from the container to prevent clogging of the valve. The propellant can be chosen from

chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorinated alkanes, and lower alkanes (C1-C5) as well as nitrous oxide dimethyl ether and other solvent-soluble propellants. Preferred propellants are lower alkanes such as propane, butane, and isobutane since these

5 result in a dramatic loss in viscosity making the formulation easy to dispense. A 70/30 mixture of propane/isobutane is a particularly preferred embodiment. In order to produce an aerosol composition the lotion is first formulated and charged into an appropriate pressure rated container. If convenient, the formulation may be heated above the melt temperature in order to facilitate filling. The propellant is then added

10 under pressure at approximately 2-30% preferably 3-20% by volume. The propellant may form a separate layer or may remain emulsified in the composition.

Methods of Preparation

15 The compositions used in the methods of the present invention may be prepared by a variety of techniques. For example, the process can often be as simple as adding the thickener system to the hydroalcoholic solvent at a temperature above the melting point of the emulsifiers, mixing briefly and cooling. Nevertheless, to ensure a composition of maximum stability the components are preferably

20 subjected to high shear (e.g. homogenized) for a limited time period while above the melting point of the thickener system followed by low shear mixing while cooling. The system should be mixed under high shear long enough to ensure a very small "droplet" size, however, excessive high shear mixing may result in decreased viscosity and stability.

25 The cooling rate may be important depending on the particular thickener system. Certain thickener systems can be homogenized and then allowed to cool slowly, however, rapid cooling appears beneficial for most systems.

30 The order of adding the components may also affect the stability and viscosity of the system. In general it works well to melt the mixed emulsifiers with aqueous-insoluble emollients together in one vessel. The hydroalcoholic solvent and any aqueous miscible emollients are mixed in a second vessel. Both components are

heated above the melting temperature of the thickener system. The hot liquid components are mixed together rapidly followed by approximately 1 to 5 minutes of homogenization for typical batches under 500 grams. While still low in viscosity the system is stirred using moderate agitation and cooled. It is also possible to add the 5 molten thickener system along with any solvent insoluble emollients to hot water (i.e., water at a temperature above the melting temperature) followed by high shear mixing and subsequent dilution with alcohol. The processing variables including amount and intensity of high shear mixing, rate of cooling, and order of addition are easily determined by one skilled in the art.

10

Test Methods

Viscosity

In the following Examples (except where indicated) viscosity was measured at 23°C at ambient pressure using a Brookfield LVDV-I[†] viscometer 15 equipped with a model D Brookfield heliopath and T spindles B-F. The spindle and speed was chosen for each particular sample such that the viscometer was operating in the middle of its range. All samples were allowed to equilibrate at 23°C for 24 hours prior to measurement. Preferably the viscosity is taken at the lowest speed possible while staying within 20-80% of the viscometer range and more preferably 20 between 30-70% of the range. In all cases the sample size and container geometry was chosen to ensure that there were no wall effects. By "wall effects" it is meant the viscosity value is not affected by the container and is essentially equivalent to the viscosity taken in an infinitely large container. For this reason lower viscosity samples required a larger sample size to accommodate the larger spindles. The 25 following table outlines preferred spindles for various sample viscosities.

DO NOT RE-ENTER

Sample Viscosity	T Spindle to Use
1,000-100,000	B
10,000-200,000	C
50,000-500,000	D
100,000-1,250,000	E
500,000-3,000,000	F

The viscosity of each sample was taken as the highest relatively stable reading achieved on the first path the spindle traversed using the heliopath adapter.

5 *Stability*

The stability of samples was measured 24 hours after conditioning at ambient conditions by placing 12 ml of a formulation that formed a lotion/cream in a 15 ml graduated centrifuge tube. The tube was then centrifuged in a Labofuge B (Heraeus Sepatech GmbH, Model 2650, rotor 2150 and buckets #2101) at 3000 rpm (2275 x g when measured at the longitudinal midpoint of the sample tube) for 20 minutes at 23°C. Stability is recorded as a volume percent separation in the Examples below.

Melt Temperature (T_m)

15 The melt temperature was measured by placing approximately 15 grams sample in a 25 cubic centimeter (cc) sealed glass vial and placing the vial in a water bath. The temperature of the bath was increased periodically in discrete increments and the contents checked after approximately 1 hour at a given temperature. The melt temperature was taken as the temperature at which the 20 mixture became very low in viscosity.

Cosmetic Properties/Tactile Testing

For use in aftershaves the compositions of this invention are preferably formulated with emollients to achieve a moisturized but relatively dry 25 feel. Compositions with excessive emollients tend to be perceived as greasy. The

formulations of this invention do not provide a tacky or sticky feel even in high humidity environments throughout the application process. The invention formulations preferably yield a smooth, soft, nontacky, and moisturized feeling.

Testing of the cosmetic or tactile properties of the compositions was conducted with

5 preferably greater than ten evaluators who applied a premeasured amount of product, approximately 2 mL. Since hand washing can affect the feel of the compositions, evaluators washed thoroughly with IVORY Skin Cleansing Liquid Gel hand soap available from Procter and Gamble, Cincinnati, OH before applying the sample.

After drying, the composition was rubbed uniformly over the surfaces of both hands

10 until the composition was dry. The feel of the composition on the skin during subsequent washing with soap and water was also important. Approximately 30-60 minutes after application of the composition the feel during subsequent washing was evaluated. Preferred formulations did not result in an abnormal feeling such as slimy, slippery, or sticky characteristics.

15

EXAMPLES

The following Examples are provided to illustrate the invention and are not intended to limit the scope of the invention.

20

Examples 1-20

The following after-shave lotion formulations were prepared using the compounds listed below in the percentages indicated in Table 1.

Table 1. Amount of ingredients in formulations

Ingredient Number	Ingredient	No Fragrance	0.25% Fragrance	0.50% Fragrance
		Wt. Percent	Wt. Percent	Wt. Percent
Part A				
1	Beheneth Ether ¹ (BB-10)	1.50	1.50	1.50
2	UNITHOX 470 ²	0.25	0.25	0.25
3	Behenyl Alcohol ³ (BE-22)	1.10	1.10	1.10
4	Cetyl Palmitate ⁴	0.05	0.05	0.05
5	Diisopropyl Dimerate ⁵	1.00	1.00	1.00
6	Squalane ⁶	1.00	1.00	1.00
7	DIMETHICONE L45/350 ⁷	0.50	0.50	0.50
8	Miconazole nitrate ⁸	2.00	2.00	2.00
Part B				
9	Polyethylene Glycol 900 ⁹	0.95	0.95	0.95
10	Polyethylene Glycol 600 ¹⁰	0.30	0.30	0.30
11	Glycerol ¹¹	0.45	0.45	0.45
12	Purified Water	29.088	29.008	28.928
Part				
13	Ethyl Alcohol ¹²	61.812	61.642	61.472

Part				
14	Fragrance ¹³	0.000	0.250	0.500

¹Beheneth-10 as NIKKOL BB-10 available from Barnet Products Corporation, Englewood Cliffs, NJ

5 ²UNITHOX 470 available from Petrolite Specialty Polymers Group, Tulsa, OK

³Behenyl alcohol as CACHELOT BE-22 available from M. Michel & Company, Inc, New York, NY

⁴Cetyl palmitate as CRODAMOL CP available from Croda, Inc. Parsippany, NY

⁵Diisopropylidineolate as PRIPURE 3786 from Unichema North America, Chicago,

10 IL

⁶Squalane as PHYTOLANE from Barnet Products Corporation, Englewood Cliffs, NJ

⁷DIMETHICONE L45/350 from OSI Specialties, Inc., Danbury, CT

⁸Antifungal from NAPP Technologies, Saddlebrook, NJ

15 ⁹Polyethylene glycol 900 from Dow Chemical, Midland, MI

¹⁰Polyethylene glycol 600 as Carbowax 600 from Union Carbide

¹¹Glycerol as. OPTIM from Dow Chemical, Midland, MI

¹²Ethanol was 190 proof from Aaper, Shelbyville, KY

¹³ See Table 2 from Intercontinental Fragrances, Houston, TX

20

Each formulation was prepared by placing the ingredients of Part A into a 200 ml glass jar and heating to 90°C for an hour to melt the emulsifiers with constant stirring. If the emulsifiers were not melted, a heat gun was applied with constant stirring. At the same time ingredients of Part B were placed into another 25 200 ml glass jar and heated to 85°C for an hour. Next Part B was added to Part A and the mixture was sheared on a Silverson homogenizer at high (100%) speed for one minute. The glass jar was sealed with a screw cap and heated to 56°C for approximately one hour. This was cooled while rolling slowly on its side for

approximately one hour. Part C was placed in a 200 ml jar and slowly added to the cooled combined formulation and shaken vigorously by hand for 60 seconds or until homogenous. The entire formulation was sheared again on the homogenizer at high speed (100%) for one minute. The steps of shaking and shearing were repeated.

5 This was allowed to cool and the formulation was centrifuged by placing it in a 250 ml centrifuge bottle and spinning at low speed, e.g., less than 500 rpm to remove air bubbles.

Twenty formulations were prepared using 5 different fragrances (Part D) at two levels of concentration (0.25% and 0.50%) and adding each at different 10 times in the preparation of the emulsion either before addition of component of Part C (Pre) or after the emulsion was completely made (post). In the latter case the fragrance was added and mixed in by vigorous shaking by hand. Table 2 contains a list of the fragrances and their descriptions.

Table 2 Description of Fragrances		
Number	Fragrance	Chemical Nature
EXP 29980	Grape	aldehydes and esters
FG 0540	Tea rose	fragrance alcohols
FG 0124	Synthetic spearmint	Hydrophobic
FG 0653	Lemon	terpenic hydrocarbons
FG 9494	Water soluble lemon	Hydrophilic

15

The stability of samples was measured after conditioning 24 hours at ambient conditions following the procedure described under Stability and recorded in Table 3. As used in Table 3 "trace" means that there was a slight settling on the bottom of the tube but this was less than 0.1 ml.

20

Table 3. Results of the Stability Test

Example Number	Fragrance Number	Before or After Component C	Fragrance (Wt. Percent)	Percent Separation
1	FG0653	Post	0.50	Trace
2	FG0124	Post	0.50	Trace
3	FG0540	Post	0.50	Trace
4	EXP29980	Post	0.50	Trace
5	FG9494	Post	0.50	Trace
6	FG0653	Post	0.25	Trace
7	FG0124	Post	0.25	Trace
8	FG0540	Post	0.25	Trace
9	EXP29980	Post	0.25	Trace
10	FG9494	Post	0.25	Trace
11	FG0653	Pre	0.25	Trace
12	EXP29980	Pre	0.25	Trace
13	FG0540	Pre	0.25	None
14	FG9494	Pre	0.25	None
15	FG0124	Pre	0.25	None
16	FG0540	Pre	0.50	Trace
17	EXP29980	Pre	0.50	Trace
18	FG9494	Pre	0.50	Trace
19	FG0653	Pre	0.50	None
20	FG0124	Pre	0.50	Trace

The results indicated that all of the fragrances produced stable emulsions. The wide variety of chemical functionality on the fragrances did not appear to effect the stability at the concentrations used. The formulations left a pleasant characteristic odor when dry. These samples demonstrate the use of both an antimicrobial agent and a fragrance. Similar results would be expected without the

antimicrobial agent (miconazole nitrate). These formulations are useful in a broad range of cosmetic products applied to the skin including shaving creams, gels, and lotions as well as after shave creams, lotions, and gels for use before, during or after removal of both facial and non-facial hair. The formulations could also be supplied 5 in the form of a mousse by introduction of a propellant as described previously.

Example 21: Alkyl Alcohol/Quaternary Amine Thickener System

The following formulations were prepared using LANETTE 22 (Henkel Corp of Ambler, PA), behenyl alcohol available under the trade designation 10 NIKKOL CA-2580 (Barnet Products Corp., Paterson, NJ), behenyltrimethyl ammonium chloride

Component	Composition		
	A	B	C
	Amount (grams)		
NIKKOL CA-2580	0.59	0.59	0.44
LANETTE 22	1.5	2.00	1.63
68:32 Ethanol:water	47.91	47.41	47.93

The compositions were prepared by separately heating the solvent and 15 the thickener system to 65-70°C. The solvent was rapidly added to the thickener system followed by stirring with an overhead paddle stirrer with the glass container immersed in a 10°C water bath. Each composition was mixed for 4.5 minutes after which the compositions cooled sufficiently for the emulsifiers to solidify.

All three compositions were viscoelastic. The samples appeared 20 pearlescent with macroscopically obvious crystalline regions. The crystals appeared macroscopically lamellar in nature. A small amount of syneresis was seen on standing at 23°C overnight. The Tm of sample C was approximately 47°C. (The sample did not melt uniformly and even at 47°C still had some solid regions.)

While in accordance with the patent statutes, description of the 25 preferred weight fractions, processing conditions, and product usages have been provided, the scope of the invention is not intended to be limited thereto or thereby.

Various modifications and alterations of the present invention will be apparent to those skilled in the art without departing from the scope and spirit of the present invention. The Examples described in this application are illustrative of the possibilities of varying the type, quantity and ratio of composition as well as the 5 methods for making formulations of the present invention. The complete disclosures of all patents, patent applications, and publications recited herein are incorporated by reference, as if individually incorporated by reference.

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